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(54) Title: GOLF BALL COMPOSITIONS			
(57) Abstract  The present invention is directed to a golf ball and a to a process for forming a golf ball having at least one layer, where the layer is formed of a saponified polymer/metallocene catalyzed polymer blend, having from about 1 to about 99 parts of at least one saponified polymer and from about 99 to 1 parts of at least one metallocene catalyzed polymer, based on 100 parts by weight of the saponified polymer/metallocene catalyzed polymer blend. The layer may be foamed or unfoamed, and may form at least a portion of any of the cover, the core, or a mantle layer situated between the cover and the core.			

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### GOLF BALL COMPOSITIONS

This application is a continuation-in-part of U.S. Application Serial No. 08/560,763, filed on November 21, 1995, and a continuation-in-part of U.S. Application Serial No. 08/950,197, filed on November 14, 1997, which is a continuation-in-part of U.S. Application Serial No. 08/658,338, filed on June 5, 1996, which is a continuation-in-part of U.S. Application Serial No. 08/482,514, filed on June 7, 1995, now U.S. Patent No. 5,703,166, which is a continuation-in-part of U.S. Application Serial No. 08/377,553 filed January 24, 1995 (now abandoned). Each of these patents is incorporated herein in its entirety by reference.

15

### FIELD OF THE INVENTION

The present invention relates to golf balls and, in particular, to golf balls having at least one layer comprising a blend of at least one saponified polymeric material and at least one polyolefin polymer produced using a single-site metallocene catalyst in the polymerization process. The metallocene catalyzed polymer may be unmodified, or may contain at least one pendant functional group that is grafted to the polymer chain by a post-polymerization reaction. The layer, which may be foamed or unfoamed, may be located in any of the cover or core of the ball or in a mantle layer located between the cover and the core.

30

### BACKGROUND OF THE INVENTION

Three-piece, wound golf balls with balata covers are preferred by most expert golfers. These balls provide a combination of distance, high spin rate, and control that is not available with other types of golf balls. However, balata is easily damaged in normal play, and, thus, lacks the durability required by the average golfer.

In contrast, amateur golfers typically prefer a solid, two-piece ball with an ionomer cover, which provides a combination of distance and durability. Because of the hard ionomer cover, these balls are almost impossible to cut, but  
5 also have a very hard "feel", which may golfers find unacceptable, and a lower spin rate, making these balls more difficult to draw or fade. The differences in the spin rate can be attributed to the differences in the composition and construction of both the cover and the core.

10 Many attempts have been made to produce a golf ball with the control and feel of a wound balata ball and the durability of a solid, two-piece ball, but none have succeeded totally. In various attempts to produce an ideal golf ball, the golfing industry has blended hard ionomer  
15 resins (i.e., those ionomer resins having a hardness of about 60 to 66 on the Shore D scale, as measured in accordance with ASTM method D-2240) with a number of softer polymeric materials, such as softer polyurethanes. However, the blends of the hard ionomer resins with the softer polymeric  
20 materials have generally been unsatisfactory in that these balls exhibit numerous processing problems. In addition, the balls produced by such a combination are usually short on distance.

While different blend combinations of species of  
25 one variety of polymer, such as prior art ionomers, i.e., copolymers of an olefin and an  $\alpha,\beta$ -unsaturated carboxylic acid, have been successfully used in the prior art, different polymers, such as carboxylic acid based ionomers and balata or other non-ionic polymers have not been successfully  
30 blended for use in golf ball covers. In general, prior art blends of polymer components are immiscible, i.e., heterogeneous on a microscopic scale, and incompatible, i.e., heterogeneous on a macroscopic scale, unless strong  
interactions are present between the polymer components in  
35 the mixture, such as those observed between carboxylic acid based ionomers and other polymers containing carboxylic acid groups. In particular, this lack of compatibility exists

when an ionomer is blended with a polyolefin homopolymer, copolymer, or terpolymer that does not contain ionic, acidic, basic, or other polar pendant groups, and is not produced with a metallocene catalyst. These mixtures often have poor  
5 tensile strength, impact strength, and the like. Hence, the golf balls produced from these incompatible mixtures will have inferior golf ball properties such as poor durability, cut resistance, and so on. In contrast, a compatible blend may be heterogeneous on a microscopic scale, but is  
10 homogeneous on a macroscopic scale, and, thus, has useful golf ball properties.

In this regard, U.S. Patent No. 5,397,840 discloses golf ball covers including a blend of "ionic copolymers" and "non-ionic copolymers". However, the "ionic copolymers" are  
15 defined as copolymers of an  $\alpha$ -olefin and a metal salt of an  $\alpha\beta$ -unsaturated carboxylic acid, and the "non-ionic copolymers" are copolymers or terpolymers containing ethylene or propylene and acrylic or methacrylic acid monomers. Therefore, strong interactions exist between the metal salts  
20 of the "ionic copolymers" and the acrylic or methacrylic acid monomers of the "non-ionic copolymers" that allow compatible blends to be formed. These interactions do not exist in prior art blends of ionomers and polymers that are truly non-ionic or nonpolar, in particular, those polymers produced  
25 with a process that does not involve the use of a metallocene catalyst.

The use of single-site metallocene catalysts in the polymerization of polyolefins produces polymers with a narrow molecular weight distribution and uniform molecular  
30 architecture, so that the order and orientation of the monomers in the polymer, and the amount and type of branching is essentially the same in each polymer chain. The narrow molecular weight distribution and uniform molecular architecture provides metallocene polymers with properties  
35 that are not available with conventional polymers, and allow polymers to be produced having unique properties that are specifically tailored to a particular application. The

desired molecular weight distribution and the molecular architecture are obtained by the selection of the appropriate metallocene catalyst and polymerization conditions. The properties may then be further tailored to an application by  
5 grafting an appropriate functional group to the polymer chain using a post-polymerization reaction.

Grafted metallocene catalyzed polymers, which are available commercially, share the advantages of unmodified metallocene catalyzed polymers, including a narrow molecular  
10 weight distribution and uniform molecular architecture. The addition of functional groups to the metallocene catalyzed polymers by grafting allows polymers to be produced having properties that are not available with unfunctionalized metallocene catalyzed polymers or polymers formed without the  
15 use of metallocene catalysts.

As shown in co-pending patent application no. 08/482,514, metallocene catalyzed polymers and ionomers form compatible blends having useful golf ball properties. However, there is no known disclosure of golf balls  
20 comprising compatible blends of grafted or non-grafted metallocene catalyzed polymers, i.e., polymers produced using single-site metallocene catalysts, and ester based ionomeric polymers produced by carrying out a hydrolysis or saponification on copolymers containing pendant ester groups  
25 to form an ionomeric polymer that is less hydrophilic than typical carboxylic acid based ionomers.

Hydrolysis or saponification of alkyl acrylate units in a crosslinkable polymer chain is disclosed by Gross in U.S. Patent No. 3,926,891. This is accomplished by  
30 dissolving the polymer in an aqueous alkali metal hydroxide solution and then heating. The product is recovered by coating the solution onto a substrate and evaporating the water or by extruding the solution into a non-solvent. In U.S. Patent No. 3,970,626, Hurst discloses heating a mixture  
35 of an alkali metal hydroxide, a thermoplastic ethylene-alkyl acrylate copolymer and water to saponify the acrylate units and form an aqueous emulsion. This emulsion can be used as

such, partially dried to a paste or moist solid, or fully dried to solid form.

A different approach to hydrolysis or saponification of an ethylene-alkyl acrylate copolymer is disclosed by Kurkov in U.S. Patent No. 5,218,057, in which the copolymer is mixed with an aqueous solution of an inorganic alkali metal base at a temperature sufficient for saponification to take place and at which the copolymer undergoes a phase change. Typically, the copolymer would be molten when mixed with the aqueous solution.

All of these prior methods require that the polymer component be in contact with water, either by conducting the reaction in an aqueous medium or by adding an aqueous solution to the polymer. Processes of this nature pose several disadvantages, however. First, it is difficult to remove water from the hydrolyzed or saponified polymer product. The polymer product is in the form of a salt that has a more polar nature than the reactant acrylate ester, and so is more likely to associate with or hydrogen bond to a polar solvent like water. The energy required to remove a highly interacting polar solvent like water is much greater than for a nonpolar or weakly polar organic solvent. Second, it is important to remove water from the ionomer product because the presence of water can have detrimental effects on ionomer mechanical properties imparted by the polar ionic domains, which act as the effective crosslink sites. Residual water weakens the ionic interactions within these domains, thereby reducing the mechanical property benefits the domains impart. Finally, incomplete removal of water can lead to difficulty in later fabricating steps where the product ionomer is reheated and shaped, e.g., into golf ball covers. Residual water can cause undesirable irregularities and imperfections on the surface of fabricated articles by the formation of blisters. Residual water within fabricated polymer articles can lead to void formation and even uncontrolled foaming with a concomitant undesirable influence

on the mechanical properties, load bearing capacity and durability of the fabricated articles.

Melt state neutralization of an ethylene-acrylic acid copolymer by a solid, solution or slurry of an alkali metal salt is disclosed by Walter in U.S. Patent No. 3,472,825. In the examples provided, hydrolysis is accomplished by mixing an alkali hydroxide with copolymer at constant temperature either in a Banbury mixer or on a two roll mill. Walter does not disclose the use of extrusion type polymer processing apparatus for this neutralization.

McClain, in U.S. Patent No. 4,638,034, discloses a process whereby ethylene-acrylic acid copolymers or their ionomers are prepared from ethylene-alkyl acrylate copolymers by saponifying the latter in the melt with metal hydroxides to form an ionomer and a by-product, i.e., alkanol, then optionally acidifying the ionomer to form the free acid copolymer. This process proceeds in the molten state and in the absence of solvent or water, other than the by-product alkanol. Saponification proceeds under non-static mixing conditions, typically with equipment commonly employed in the art of mixing molten polymer materials such as multiroll mills, a Banbury mixer or a twin screw extruder.

The process disclosed by the '034 reference is, however, incapable of providing optimal product quality since blending and saponifying in a single operation as taught by the subject reference leads to rapid hydrolysis, with a concurrent rapid increase in viscosity. Due to this rapid increase in viscosity, the resultant mixture is non-uniform and therefore the physical properties of products made from this material are not consistent throughout the product.

During the melt state conversion of the alkyl-acrylate copolymer to the metal acrylate copolymer salt, a great decrease in melt flow rate occurs with a corresponding great increase in melt viscosity. While not wishing to be bound by any particular theory, this decreased melt flow rate is thought to occur because of the tendency of the relatively polar ionic salt functionalities formed during



the saponification reaction to associate with themselves rather than the relatively nonpolar unreacted alkyl acrylate or comonomer chain segments. Aggregations of salt moieties arising from side groups attached to different chains into 5 ionic domains introduces effective crosslink points throughout the molten copolymer. The effective crosslinks, in turn, greatly increase the copolymer melt viscosity and, correspondingly, greatly decrease copolymer melt flow rate.

A need exists in the golf ball art for highly 10 durable golf balls, which have improved performance, and may be tailored to have virtually any combination of feel and spin rate. The present invention provides such a golf ball.

### Summary of the Invention

15 The present invention is directed to a golf ball having least one layer, where the layer formed of a saponified polymer/metallocene catalyzed polymer blend, comprising from about 1 to about 99 parts of at least one saponified polymer and from about 99 to 1 parts of at least 20 one metallocene catalyzed polymer, based on 100 parts by weight of the saponified polymer/metallocene catalyzed polymer blend. The layer may be foamed or unfoamed, and may form at least a portion of any of the cover, the core, or a mantle layer situated between the cover and the core.

25 Preferred metallocene catalyzed polymers include olefinic homopolymers, such as polyethylene, and copolymers of ethylene with propylene, butene, hexene, octene, and norbornene, and olefinic homopolymers and copolymers of propylene with butene, hexene, octene, and norbornene.

30 However, the metallocene catalyzed polymer may be any metallocene catalyzed polymer of the formula:

wherein

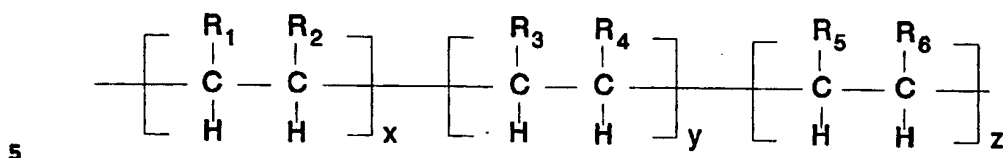
$R_1$  is hydrogen;

$R_2$  is hydrogen or lower alkyl selected from the group

35 consisting of  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$ ,  $\text{C}_4\text{H}_9$ , and  $\text{C}_5\text{H}_{11}$ ;

$R_3$  is hydrogen or lower alkyl selected from the group

consisting of  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$ ,  $\text{C}_4\text{H}_9$ , and  $\text{C}_5\text{H}_{11}$ ;



- $R_4$  is selected from the group consisting of H,  $CH_3$ ,  $C_2H_5$ ,  $C_3H_7$ ,  $C_4H_9$ ,  $C_5H_{11}$ ,  $C_6H_{13}$ ,  $C_7H_{15}$ ,  $C_8H_{17}$ ,  $C_9H_{19}$ ,  $C_{10}H_{21}$ , and phenyl, in which from 0 to 5 H within  $R_4$  can be replaced by substituents
- 10 selected from the group consisting of  $COOH$ ,  $SO_3H$ ,  $NH_2$ , F, Cl, Br, I, OH, SH, silicone, lower alkyl esters and lower alkyl ethers, with the proviso that  $R_3$  and  $R_4$  can be combined to form a bicyclic ring;
- $R_5$  is hydrogen, lower alkyl including  $C_1$ - $C_3$ , carbocyclic,
- 15 aromatic or heterocyclic;
- $R_6$  is hydrogen, lower alkyl including  $C_1$ - $C_3$ , carbocyclic, aromatic or heterocyclic; and
- wherein x ranges from 99 to 50 weight per cent of the polymer, y ranges from 1 to 50 weight per cent of the polymer
- 20 and z ranges from 0 to 49 weight per cent of the polymer.

The saponified polymer typically comprises a first olefinic, monomeric component having from 2 to 8 carbon atoms and a second monomeric component comprising an unsaturated carboxylic acid based acrylate class ester having from 4 to

25 22 carbon atoms and at least one ester group, wherein at least a portion of the ester groups have been saponified with an inorganic metal base. Useful inorganic metal bases include, but are not limited to metal bases comprising at least one metallic cation, such as lithium, sodium,

30 potassium, cesium, magnesium, calcium, barium, manganese, copper, zinc, aluminum, titanium, tungsten, zirconium, platinum, rubidium, and strontium, and at least one anion, such as hydroxide, alkoxide, acetate, carbonate, bicarbonate, oxide, formate, and nitrate.

35

Typically, the first monomeric component is an  $\alpha$ -olefin monomer having a terminal point of unsaturation, and may be of the formula:



where  $\text{R}_7$  is hydrogen or an alkyl group, and  $\text{R}_8$  is hydrogen, lower alkyl including  $\text{C}_1\text{--C}_5$ , carbocyclic, aromatic or heterocyclic. Preferably, the first monomeric component is ethylene.

Typically, the first monomeric component comprises from about 1 to about 99 percent by weight of the total polymer weight, preferably from about 10 to about 95 percent by weight of the total polymer weight, and most preferably from about 10 to about 70 percent by weight of the total polymer weight.

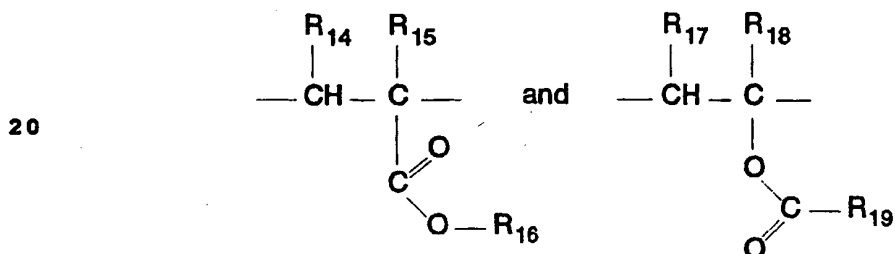
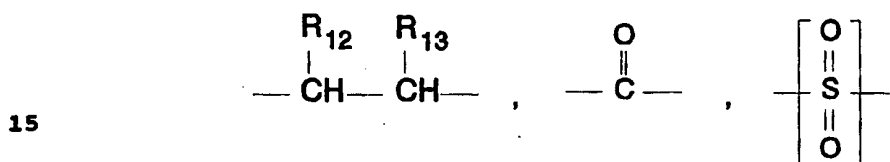
The second monomeric component is typically an unsaturated acrylate class ester having the formula:



25 where  $\text{R}_9$  is hydrogen or an alkyl group;  $\text{R}_{10}$  is hydrogen, lower alkyl including  $\text{C}_1\text{--C}_5$ , carbocyclic, aromatic or heterocyclic;  $\text{R}_{11}$  is selected from the group consisting of  $\text{C}_n\text{H}_{2n+1}$ , for  $n=1$  to 18 and phenyl, in which from 0 to 5 H within  $\text{R}_{10}$  can be replaced by substituents selected from the group consisting of  $\text{COOH}$ ,  $\text{SO}_3\text{H}$ ,  $\text{NH}_2$ , succinic anhydride and their salts, F, Cl, Br, I, OH, SH, epoxy, silicone, lower alkyl esters, lower alkyl ethers, and aromatic or heterocyclic rings with the proviso that  $\text{R}_{10}$  and  $\text{R}_{11}$  can be combined to form a bicyclic ring. Typically, the second monomeric component comprises from about 99 to about 1 percent by weight of the total

polymer weight, preferably, from about 90 to about 5 percent by weight of the total polymer weight, and most preferably, from about 90 to about 30 percent by weight of the total polymer weight.

5 The saponified polymer may also comprise a third monomeric component. Useful third monomeric components include carbon monoxide, sulfur dioxide, an anhydride monomer, an unsaturated monocarboxylic acid, an olefin having from 2 to 8 carbon atoms and a vinyl ester or a vinyl ether  
 10 of an alkyl acid having from 4 to 21 carbon atoms. Preferred third monomeric components include monomers of formula



25

wherein:

$\text{R}_{12}$  is hydrogen, lower alkyl including  $\text{C}_1\text{--C}_5$ , carbocyclic, aromatic or heterocyclic;

30  $\text{R}_{13}$  is hydrogen, lower alkyl including  $\text{C}_1\text{--C}_5$ , carbocyclic, aromatic or heterocyclic;

$\text{R}_{14}$  is hydrogen, lower alkyl including  $\text{C}_1\text{--C}_5$ , carbocyclic, aromatic or heterocyclic;

$\text{R}_{15}$  is hydrogen or lower alkyl including  $\text{C}_1\text{--C}_5$ ;

35  $\text{R}_{16}$  is hydrogen, or is selected from the group consisting of  $\text{C}_n\text{H}_{2n+1}$ , for  $n=1$  to 18 and phenyl, in which from 0 to 5 H within  $\text{R}_{16}$  can be replaced by substituents

selected from the group consisting of COOH, SO<sub>3</sub>H, NH<sub>2</sub> and their salts, F, Cl, Br, I, OH, SH, silicon, lower alkyl esters, lower alkyl ethers and aromatic or heterocyclic rings with the proviso that R<sub>15</sub> and R<sub>16</sub> can be combined to form a bicyclic ring;

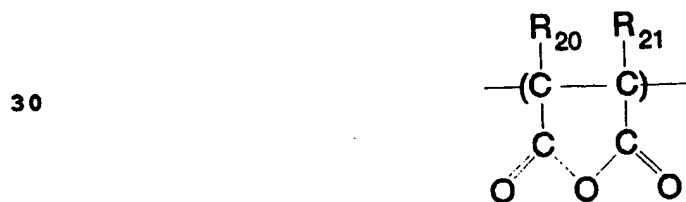
R<sub>17</sub> is hydrogen, lower alkyl including C<sub>1</sub>-C<sub>5</sub>, carbocyclic, aromatic or heterocyclic;

R<sub>18</sub> is hydrogen or lower alkyl including C<sub>1</sub>-C<sub>5</sub>;

R<sub>19</sub> is hydrogen, or is selected from the group consisting of C<sub>n</sub>H<sub>2n+1</sub>, for n=1 to 18 and phenyl, in which from 0 to 5 H within R<sub>19</sub> can be replaced by substituents selected from the group consisting of COOH, SO<sub>3</sub>H, NH<sub>2</sub> and their salts, F, Cl, Br, I, OH, SH, epoxy, silicon, lower alkyl esters, lower alkyl ethers and aromatic or heterocyclic rings with the proviso that R<sub>18</sub> and R<sub>19</sub> can be combined to form a bicyclic ring.

Typically, the third monomeric component comprises from about 0 to 49 percent by weight of the total polymer weight of the saponified polymer. The monomeric components of the polymer may be present in a random, alternating, block or graft arrangement, and the saponified polymers may be isotactic, syndiotactic, atactic polymers, or a combination thereof.

A grafting agent may also be added to at least one of the saponified polymer or the metallocene catalyzed polymer to form a grafted polymer. The preferred grafting agent is an anhydride having the formula:



where R<sub>20</sub> and R<sub>21</sub> are the same or different, and are typically hydrogen, linear or branched chain alkyl, or substituted or unsubstituted carboxylic groups.

The grafting agent is typically added in an amount of between about 1 to about 50 percent by weight, preferably from about 1 to about 25 percent by weight, and most preferably from about 1 to about 15 percent by weight of the  
5 polymer.

The present invention is also directed to a process for forming a golf ball, which comprises forming a polymer comprising a first olefinic monomeric component having from 2 to 8 carbon atoms and a second monomeric component comprising  
10 an unsaturated carboxylic acid based acrylate class ester having from 4 to 22 carbon atoms; applying a sufficient amount of heat to the polymer to convert the polymer to a substantially molten state; forming a mixture by adding an inorganic metal base to the molten polymer, such that the  
15 viscosity of the mixture remains substantially unchanged from the viscosity of the molten polymer; saponifying the mixture to form a saponified polymer, where a sufficient amount of the inorganic metal base is added to the molten polymer in forming the mixture to obtain a degree of saponification of  
20 the polymer ranging between about 1 and 50 percent. The saponified polymer is then blended with a metallocene catalyzed polymer to form a saponified polymer/metallocene catalyzed polymer blend, which is used to form at least one layer of a golf ball. Optionally, the polymer further  
25 comprises a third monomeric component, such as carbon monoxide, sulfur dioxide, an anhydride monomer, an unsaturated monocarboxylic acid, an olefin having from 2 to 8 carbon atoms, or a vinyl ester or a vinyl ether of an alkyl acid having from 4 to 21 carbon atoms.

30

#### Detailed Description of the Invention

As used herein, the term "metallocene catalyzed polymer" refers to any polymer, copolymer, or terpolymer, and, in particular, any polyolefin, polymerized using a  
35 metallocene catalyst. The term "grafted metallocene catalyzed polymer" refers to any metallocene catalyzed polymer in which the metallocene catalyzed polymer has been

subjected to a post-polymerization reaction to graft at least one functional group onto the metallocene catalyzed polymer. Similarly, the term "non-grafted metallocene catalyzed polymer" refers to any metallocene catalyzed polymer in which  
5 the metallocene catalyzed polymer has not been subjected to such a post-polymerization reaction. Accordingly, the term "metallocene catalyzed polymer" encompasses both non-grafted metallocene catalyzed polymers and grafted metallocene catalyzed polymers.

10 As used herein, the terms "saponified polymer" and "saponified ionomer" refer to a polymer comprising at least one olefin and at least one unsaturated monomer that contains a pendant ester group, where at least some of the pendant ester groups have been hydrolyzed or saponified. Saponified  
15 ionomers differ from prior art ionomers in that any pendant groups that are not modified by the saponification process are ester groups in contrast to the pendant carboxylic acid groups that remain after neutralization in prior art ionomers.

20 The terms "saponified polymer/metallocene catalyzed polymer blend" and "saponified/metallocene catalyzed polymer blend", as used herein, refers to any polymer blend that comprises at least one saponified polymer and at least one grafted or non-grafted metallocene catalyzed polymer.

25 As used herein, the term "layer" includes any generally spherical portion of a golf ball or golf ball core, center, or mantle, including one-piece cores and one-piece balls. A "mantle" is defined herein as a portion of the golf ball that occupies a volume between the cover and the core.  
30 Of course, as one of ordinary skill in the art would recognize, any of the core, cover, and mantle of the golf balls of the invention can be formed of one layer or a plurality of layers, as that term is defined herein.

In addition, as used herein with regard to a  
35 polymer blend, the term "compatible" refers to a blend of two or more polymers, having useful golf ball properties, that is homogeneous on a macroscopic scale. Compatible blends may be

miscible, i.e., homogeneous on a microscopic scale, or at least partially immiscible, i.e., heterogeneous on a microscopic scale, but homogeneous on a macroscopic scale. The term "incompatible" refers to a mixture of at least two  
5 polymers that is heterogeneous on both a microscopic scale and a macroscopic scale, such that useful golf ball properties, such as durability, are lacking.

The present invention relates to golf balls including at least one foamed or unfoamed layer that  
10 comprises a compatible blend of at least one saponified polymer and one or more grafted or non-grafted metallocene catalyzed polymers, i.e., a saponified polymer/metallocene catalyzed polymer blend. As noted above, the layer may be in any of the core, the cover, or a mantle layer situated  
15 between the cover and the core.

Saponified polymer/metallocene catalyzed polymer blends useful in the invention typically comprise at least one layer of a compatible blend of at least one grafted or non-grafted metallocene catalyzed polymer and at least one  
20 saponified polymer, typically from about 1 to about 99 parts of the metallocene catalyzed polymer and from about 99 to about 1 parts of the saponified polymer, preferably from about 5 to about 90 parts of at least one metallocene catalyzed polymer and about 95 to about 10 parts of at least  
25 one saponified polymer, more preferably from about 10 to about 75 parts of at least one metallocene catalyzed polymer and about 90 to about 25 parts of at least one saponified polymer, and most preferably from about 10 to about 50 parts of at least one metallocene catalyzed polymer and about 90 to  
30 about 50 parts of at least one saponified polymer, based on 100 parts by weight of saponified polymer/metallocene catalyzed polymer blend. Typically, the layer has a thickness of from about 0.005 to about 0.125 inch and a Shore D hardness of from about 15 to about 80. Where the layer is  
35 foamed, the polymer blends may be foamed during molding by any conventional foaming or blowing agent. Preferably, foamed layers incorporating a saponified polymer/metallocene



catalyzed polymer blend have a flexural modulus of from about 1000 to about 150,000 psi.

Compatible blends in accordance with the invention, comprising saponified polymers and metallocene catalyzed polymers, may be thermoformed, and, thus, can be either compression or injection molded to form a layer of foamed or unfoamed saponified polymer/metallocene catalyzed polymer blend in the cover, core, or mantle of a golf ball according to the invention. Blends of grafted or non-grafted metallocene catalyzed polymers and saponified polymers are resilient, easily processed materials that allow highly durable golf balls to be produced with improved performance and virtually any combination of feel and spin rate.

Golf balls according to the invention may incorporate cores comprising saponified polymer/metallocene catalyzed polymer blends, as well as saponified polymers or polymer blends, grafted metallocene catalyzed polymers or polymer blends, non-grafted metallocene catalyzed polymers or polymer blends, or conventional materials. Cores comprising a blend of at least one saponified polymer and at least one grafted or non-grafted metallocene catalyzed polymer may be either one-piece, comprising a single piece of foamed or unfoamed saponified polymer/metallocene catalyzed polymer blend, or multi-piece, comprising a liquid or solid core or center and one or more layers in which any of the center or at least one of the layers comprises a foamed or unfoamed blend of a saponified polymer and a grafted or non-grafted metallocene catalyzed polymer.

For example, Fig. 1 illustrates a golf ball according to the invention with a one-piece core. Golf ball 1 comprises a core 2 and a cover 3, wherein either of core 2 or cover 3 incorporates at least one layer comprising a foamed or unfoamed blend of a saponified polymer and a grafted or non-grafted metallocene catalyzed polymer blend.

Similarly, Fig. 2 illustrates a golf ball according to the invention incorporating a multi-piece core. Golf ball 10 comprises a cover 12, a core having a center 14 and at

least one additional core layer 16. Any of the cover 12, center 14, or core layer 16 may incorporate at least one foamed or unfoamed layer that comprises a saponified polymer/metallocene catalyzed polymer blend.

- 5 Conventional materials useful in centers, cores, or core layers of the golf balls of the invention include, but are not limited to, compositions having a base rubber, a crosslinking agent, and a filler. The base rubber typically includes natural or synthetic rubbers. A preferred base  
10 rubber is 1,4-polybutadiene having a cis-structure of at least 40 percent. Natural rubber, polyisoprene rubber and/or styrene-butadiene rubber may be optionally added to the 1,4-polybutadiene. Crosslinking agents include metal salts of unsaturated fatty acids, such as zinc or magnesium salts  
15 acrylic or methacrylic acid. The filler typically includes materials such as zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate and the like. Golf balls of the invention may also have conventional wound cores, where the core comprises a liquid or solid center wrapped in  
20 elastomeric windings.

- Golf balls of the invention may also include a mantle layer situated between the cover and the core. Preferably, the mantle layer comprises a least one foamed or unfoamed layer that comprises a saponified  
25 polymer/metallocene catalyzed polymer blend, but may also be formed from a saponified polymer or polymer blend, a grafted or non-grafted metallocene catalyzed polymer or polymer blend, or from any other suitable polymeric material having the desired properties, including, but not limited to, block  
30 copolymers of a poly(ether-ester), such as HYTREL®, available from DuPont, block copolymers of a poly(ether-amide), such as PEBAX®, available from Elf Atochem, and styrene-butadiene-styrene and styrene-(ethylene-propylene)-styrene or  
35 styrene-(ethylene-butylene)-styrene block copolymers, such as KRATON D® and KRATON G® from Shell Chemical.

A golf ball incorporating a mantle layer is illustrated in Fig. 3, which depicts golf ball 20, having cover 23, core 24, and a mantle layer 25 situated between the cover and the core. Any of cover 23, core 24, and mantle layer 25 may incorporate at least one layer of a foamed or unfoamed saponified polymer/metallocene catalyzed polymer blend. Moreover, core 24 may be a one-piece core, a multi-layer core, or a wound core, having a solid or liquid center.

10 Golf balls according to the invention may also incorporate cover layers comprising foamed or unfoamed saponified polymer/metallocene catalyzed polymer blends, grafted metallocene catalyzed polymers or polymer blends, non-grafted metallocene catalyzed polymers or polymer blends,  
15 or conventional materials, including balata and ionomer cover stock. Saponified polymer/metallocene catalyzed polymer blend cover layers according to the invention may be used with conventional solid or wound cores, as well as those comprising saponified polymers or grafted or non-grafted  
20 metallocene catalyzed polymers or polymer blends. Preferably, the cover of a golf ball according to the invention is formed from a blend comprising at least one grafted metallocene catalyzed polymer and at least one saponified polymer.

25 When a layer of foamed or unfoamed saponified polymer/metallocene catalyzed polymer blend is used in a golf ball cover or mantle, the ball has a softer feel than balls using a hard ionomer, and is more deformable. The increased deformation of the cover and outer layers of the ball  
30 provides improved control due to the increased "bite" on the clubface when the ball is struck, which prevents or reduces sliding of the ball up the clubface, and allows more energy to be imparted directly to the core at impact, providing a greater initial velocity. The improved control and feel are  
35 similar to those obtained using a soft balata cover without the decrease in durability that is typically associated with balata.

The use of a foamed saponified polymer/metallocene catalyzed polymer blend also allows the golf ball designer to adjust the density or mass distribution of the ball to adjust the angular moment of inertia, and, thus, the spin rate and performance of the ball. Foamed materials also offer a potential cost savings due to the reduced use of polymeric material.

As used herein with regard to saponified polymers and metallocene catalyzed polymers, the phrase "branched or straight chain alkyl" means any substituted or unsubstituted acyclic carbon-containing compounds. Examples of alkyl groups include lower alkyl, for example, methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl or tert-butyl; upper alkyl, for example, octyl, nonyl, decyl, and the like; and lower alkylene, for example, ethylene, propylene, butylene, pentene, hexene, heptene, octene, norbornene, nonene, decene and the like. The ordinary skilled artisan is familiar with numerous linear and branched alkyl groups, which are within the scope of the present invention.

In addition, such alkyl groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Functional groups include, but are not limited to hydroxyl, amino, carboxyl, sulfonic amide, ester, ether, phosphates, thiol, nitro, silane and halogen (fluorine, chlorine, bromine and iodine), to mention but a few.

As used herein, "substituted and unsubstituted carbocyclic" means cyclic carbon-containing compounds, including, but not limited to cyclopentyl, cyclohexyl, cycloheptyl, adamantyl, and the like. Such cyclic groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Such functional groups include those described above, and lower alkyl groups having from 1-28 carbon atoms. The cyclic groups of the invention may further comprise a heteroatom.

As used herein, "substituted and unsubstituted aryl groups" refers to any functional group comprising a

hydrocarbon ring having a system of conjugated double bonds, such as phenyl, naphthyl, anisyl, toluyyl, xylenyl and the like. According to the present invention, aryl also includes heteroaryl groups, e.g., pyrimidine or thiophene. These aryl groups may also be substituted with any number of a variety of functional groups. In addition to the functional groups described above in connection with substituted alkyl groups and carbocyclic groups, functional groups on the aryl groups can include nitro groups.

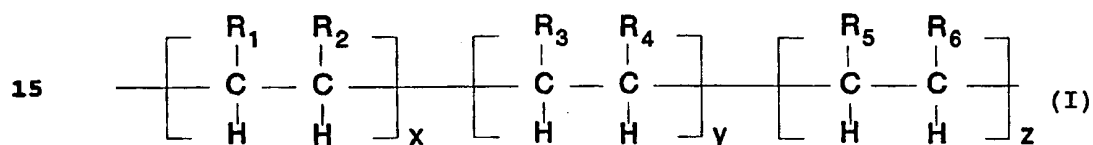
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#### Metallocene Catalyzed Polymers and Polymer Blends

The narrow molecular weight distributions of metallocene catalyzed polymers provide more uniform compositions and improved mechanical properties when compared to polyolefins polymerized with conventional catalysts. In addition, when the metallocene catalyzed polymer is modified by a post-polymerization reaction to add at least one pendant functional group to the metallocene catalyzed polymer, the compatibility of the resulting grafted metallocene catalyzed polymer with other polymers, and with ionomers, including saponified ionomers, in particular, is improved. As a result, blends of grafted metallocene catalyzed polymers and ionomers have superior golf ball properties, including performance and durability. For example, as demonstrated in the examples provided in co-pending application no. 08/950,197, a compatible blend of a grafted metallocene catalyzed polymer and an ionomer results in a golf ball cover composition that provides a higher initial velocity for a given cover hardness, when compared to covers comprising a blend of a VLMI, i.e., a very low modulus ionomer, and a second ionomer.

Grafted metallocene catalyzed polymers useful in the golf balls of the invention are available in experimental quantities from DuPont, or may be obtained by subjecting a non-grafted metallocene catalyzed polymer to a post-polymerization reaction to provide a grafted metallocene catalyzed polymer with the desired pendant group or groups.

Examples of metallocene catalyzed polymers to which functional groups may be grafted for use in the invention include, but are not limited to, homopolymers of ethylene and copolymers of ethylene and a second olefin, preferably, 5 propylene, butene, pentene, hexene, heptene, octene, and norbornene, and most preferably, propylene, butene, pentene, hexene, heptene, octene, and norbornene. Generally, the invention includes golf balls having at least one layer comprising at least one grafted metallocene catalyzed polymer 10 or polymer blend, where the grafted metallocene catalyzed polymer is produced by grafting a functional group onto a metallocene catalyzed polymer having formula I:



wherein

20  $R_1$  is hydrogen, branched or straight chain alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, and octyl, carbocyclic, aromatic or heterocyclic;

$R_2$  is hydrogen, lower alkyl including  $C_1-C_3$ ; carbocyclic, aromatic or heterocyclic

25  $R_3$  is hydrogen, lower alkyl including  $C_1-C_3$ , carbocyclic, aromatic or heterocyclic;

$R_4$  is selected from the group consisting of H,  $C_nH_{2n+1}$ , where  $n = 1$  to 18, and phenyl, in which from 0 to 5 H within  $R_4$  can be replaced by substituents selected from the 30 group consisting of  $COOH$ ,  $SO_3H$ ,  $NH_2$ , F, Cl, Br, I, OH, SH, silicone, lower alkyl esters and lower alkyl ethers, with the proviso that  $R_3$  and  $R_4$  can be combined to form a bicyclic ring;

$R_5$  is hydrogen, lower alkyl including  $C_1-C_3$ , 35 carbocyclic, aromatic or heterocyclic;

$R_6$  is hydrogen, lower alkyl including  $C_1-C_3$ , carbocyclic, aromatic or heterocyclic; and

wherein x, y and z are the relative percentages of each co-monomer. The number x can range from 1-99 percent or more preferably from 10-70 percent and most preferred, from about 10-50 percent. The number y can be from 99-1 percent, 5 preferably, from 90-30 percent, or most preferably, 90-50 percent. The number z can range from 0 to 49 percent.

Preferred grafted metallocene catalyzed polymers are formed by grafting a functional group onto a metallocene catalyzed polyethylene or a metallocene catalyzed polymer of 10 formula I in which  $R_1$  is hydrogen or lower alkenyl, and  $R_2$  is hydrogen or alkyl, including carbon chains having from 1 to 10 carbon atoms. However,  $R_1$  and  $R_2$  can represent any combination of alkyl, carbocyclic or aryl groups, for example, 1-cyclohexylpropyl, benzyl cyclohexylmethyl, 15 2-cyclohexylpropyl, 2,2-methylcyclohexylpropyl, 2,2-methylphenylpropyl, 2,2-methylphenylbutyl.

In addition,  $R_3$  is preferably hydrogen or lower alkyl or alkenyl such as carbon chains having 1-10 carbon atoms, and  $R_4$  is a lower alkyl group having from 1-10 carbon 20 atoms. For terpolymers, where z is not zero,  $R_5$  is preferably hydrogen or lower alkyl or alkenyl such as carbon chains having 1-10 carbon atoms, and  $R_6$  is a lower alkyl group having from 1-10 carbon atoms. In the most preferred copolymer,  $R_1$  and  $R_2$  are hydrogen,  $R_3$  is hydrogen, methyl, ethyl, propyl, 25 butyl, pentyl, hexyl, heptyl or octyl, and  $R_4$  is a straight carbon chain having 6 carbon atoms. For terpolymers,  $R_5$  is most preferably hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl or octyl, and  $R_6$  is a straight carbon chain having 6 carbon atoms.

30 Metallocene catalyzed copolymers or terpolymers can be random or block copolymers or terpolymers, and may be isotactic, syndiotactic or atactic. The pendant groups creating the isotactic, syndiotactic or atactic polymers are chosen to determine the interactions between the different 35 polymer chains making up the resin to control the final properties of the resins used in golf ball covers, cores, or

mantles. As will be clear to those skilled in the art, grafted metallocene catalyzed polymers useful in the invention that are formed from metallocene catalyzed random or block copolymers or terpolymers will also be random or  
5 block copolymers or terpolymers, and will have the same tacticity of the metallocene catalyzed polymer backbone.

Non-grafted metallocene catalyzed polymers useful in the present invention are commercially available under the trade name AFFINITY® polyolefin plastomers and ENGAGE®  
10 polyolefin elastomers by Dow Chemical Company and DuPont-Dow. Other commercially available metallocene catalyzed polymers can be used such as Exxon's Exact® and Dow's Insight® line of resins which have superior flexibility and clarity as well as toughness. The Exact® and Insight® line of polymers also  
15 have novel rheological behavior in addition to their other properties as a result of using a metallocene catalyst technology. Metallocene catalyzed polymers are also available from Sentinel Products Corporation of Hyannis, Massachusetts, as foamed sheets for compression molding. The  
20 foamed grafted metallocene catalyzed polymers sheets are available in thicknesses ranging from about 0.027 to 0.625 inches (0.069 to 0.159 cm). Closed cell bun stock is also available in thicknesses of up to 4 inches (10.2 cm).

Grafted metallocene catalyzed polymers,  
25 functionalized with pendant groups, such as maleic anhydride, and the like, are available in experimental quantities from DuPont.

In addition, grafted metallocene catalyzed polymers may be formed from commercially available metallocene  
30 catalyzed polymers using post-polymerization reactions known in the art. For example, the grafted metallocene catalyzed polymers may be formed using the method disclosed in EPA 0 266 994 by admixing a metallocene catalyzed polymer with a monomer capable of bonding to the metallocene  
35 catalyzed polymer and an organic peroxide, and mixing the admixture at a temperature greater than the melting point of the metallocene catalyzed polymer for a time sufficient for



the post-polymerization reaction to occur. Typically, the mixing is continued for at least four times the half-life of the organic peroxide. Although the monomer, metallocene catalyzed polymer, and the peroxide may be added in any  
5 order, preferably, the metallocene catalyzed polymer and monomer are thoroughly mixed before the peroxide is added.

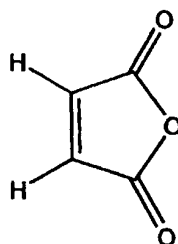
Monomers useful for grafting to metallocene catalyzed polymers include, but are not limited to, olefinic monomers having, as a functional group, sulfonic acid,  
10 sulfonic acid derivatives, such as chlorosulfonic acid, vinyl ethers, vinyl esters, primary, secondary, and tertiary amines, mono-carboxylic acids, dicarboxylic acids, partially or fully ester derivatized mono-carboxylic acids and dicarboxylic acids, and anhydrides of dicarboxylic acids, and  
15 cyclic imides of dicarboxylic acids. In polyethylene, the post-polymerization reaction results in the substitution of the monomer for a hydrogen on the polymer backbone. Because all of the secondary hydrogen atoms are equivalent in polyethylene, the pendant group may replace any of the  
20 secondary hydrogens on the polymer. In copolymers and polymers of olefins other than ethylene, which contain both secondary and tertiary hydrogens, the tertiary hydrogens are more labile, and, thus, the reaction occurs substantially exclusively at the site of the tertiary hydrogens.

25 In addition, metallocene catalyzed polymers may also be functionalized by sulfonation, carboxylation, or the addition of an amine, hydroxy, or epoxy group. Metallocene catalyzed polymers functionalized by sulfonation, carboxylation, or the addition of a hydroxy group may be  
30 converted to anionic ionomers by treatment with a base. Similarly, metallocene catalyzed polymers functionalized by the addition of an amine may be converted to cationic ionomers by treatment with an alkyl halide, acid, or acid derivative.

35 The most preferred monomer is maleic anhydride, which, once attached to the metallocene catalyzed polymer by the post-polymerization reaction, may be further subjected to

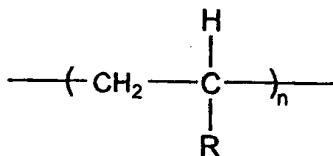
any reaction to which an anhydride may be subject to form a grafted metallocene catalyzed polymer containing other pendant or functional groups. For example, reaction with water will convert the anhydride to a dicarboxylic acid, reaction with ammonia forms an amide, reaction with an alcohol results in the formation of an ester, and reaction with base results in the formation of an anionic ionomer.

In particular, maleic anhydride, which is of formula II



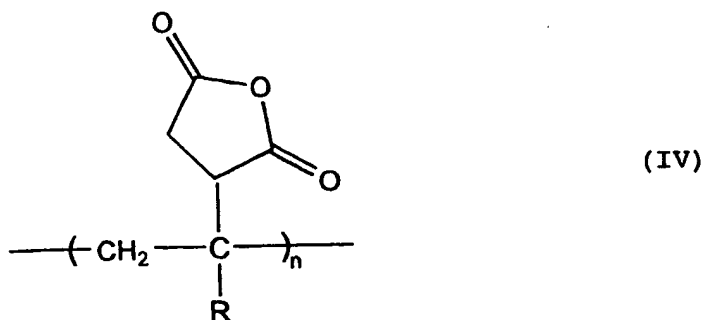
(II)

may be grafted onto a metallocene-catalyzed polymer by means of a post-polymerization reaction, as described above. The maleic anhydride will graft onto a metallocene catalyzed polymer of formula III

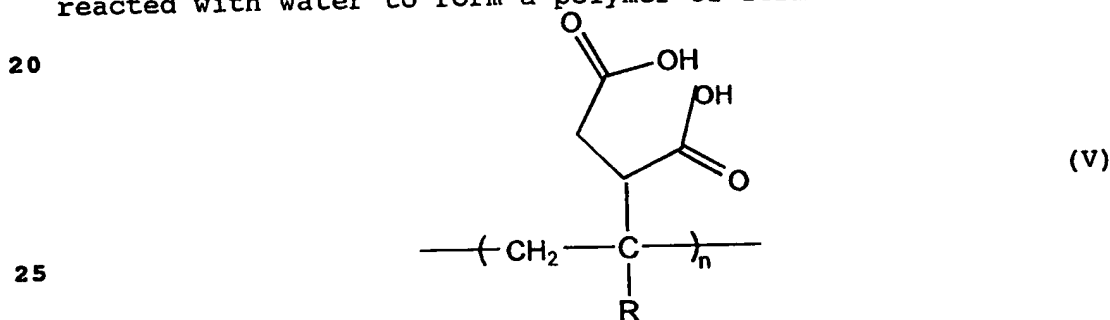


(III)

to form a grafted metallocene catalyzed polymer of formula IV



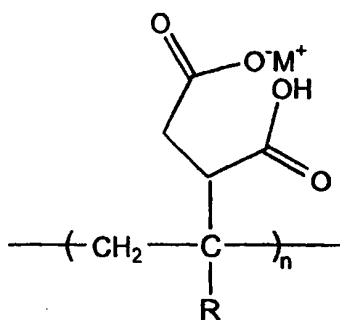
10 where R may be hydrogen, branched or straight chain alkyl, carbocyclic, aromatic or heterocyclic. Where R is not H, the monomer being grafted to the metallocene catalyzed polymer will always replace the tertiary H because the tertiary H is  
 15 more labile than the secondary H. Clearly, in polyethylene, where every H is a secondary H, the monomer must replace a secondary H. Where the monomer is a maleic anhydride, the resulting grafted metallocene catalyzed polymer may be  
 20 reacted with water to form a polymer of formula V



30 which may be further reacted with a base of formula MOH to form an ionomer of formula VI

35

5

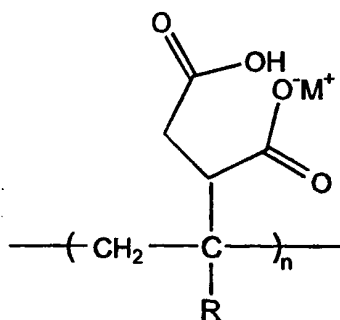


(VI)

10

formula VII

15

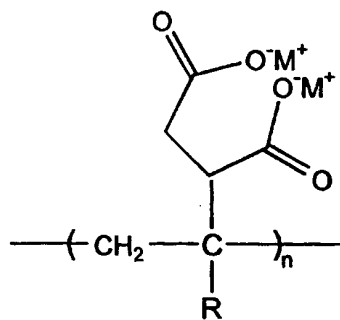


(VII)

20

or formula VIII

25

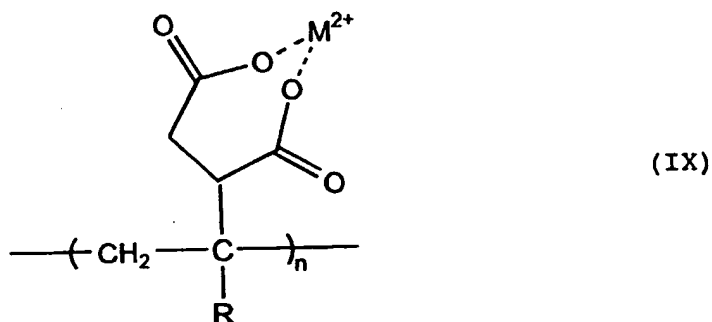


(VIII)

30

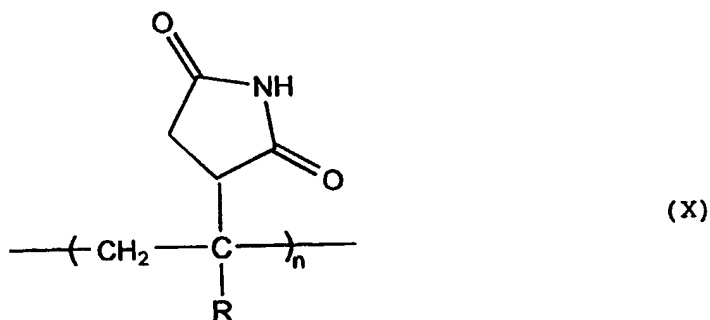
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or reacted with a base of formula  $M(OH)_2$  to form an ionomer of formula IX



where R is, as defined above, hydrogen, branched or straight chain alkyl, carbocyclic, aromatic or heterocyclic.

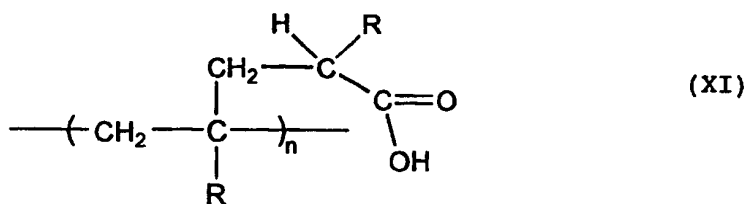
A maleic anhydride grafted metallocene catalyzed polymer may also be reacted with ammonia to form a polymer of formula X



where R is again, as defined above, hydrogen, branched or straight chain alkyl, carbocyclic, aromatic or heterocyclic.

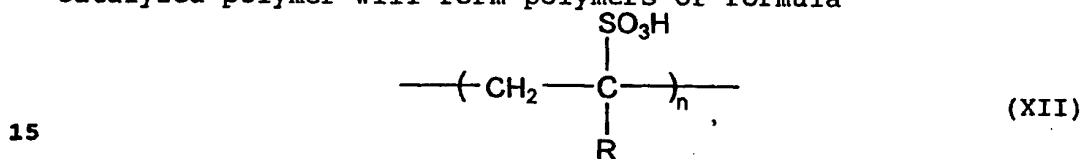
It has been discovered that maleic anhydride grafted metallocene catalyzed polymers form highly compatible blends with ionomers and other thermoplastic polymers.

In addition, unsaturated carboxylic acids, such as methacrylic and acrylic acid, can be grafted to a metallocene catalyzed polymer to form



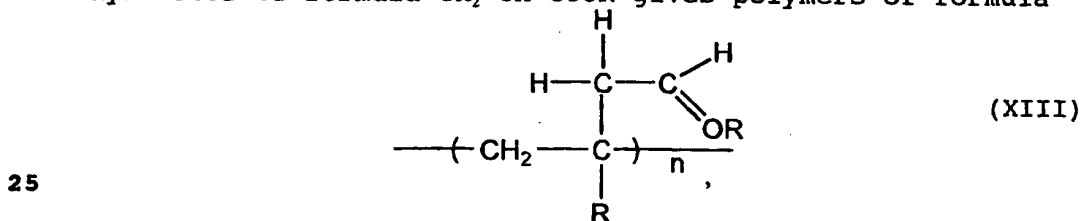
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which may be reacted with a base to form an ionomer, where R may again be hydrogen, branched or straight chain alkyl, carbocyclic, aromatic or heterocyclic. Sulfur compounds, such as  $\text{H}_2\text{SO}_4$ ,  $\text{ClSO}_3\text{H}$ , or  $\text{SO}_3$ , when grafted to a metallocene catalyzed polymer will form polymers of formula



15

where R may again be hydrogen, branched or straight chain alkyl, carbocyclic, aromatic or heterocyclic. Grafting a vinyl ester of formula  $\text{CH}_2=\text{CH}-\text{COOR}$  gives polymers of formula

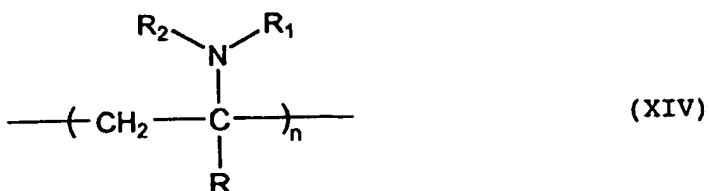


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and a primary or secondary amine or other suitable nitrogen compound provides polymers of formula

30

35



5

where R is as defined above.

If a monomer of formula

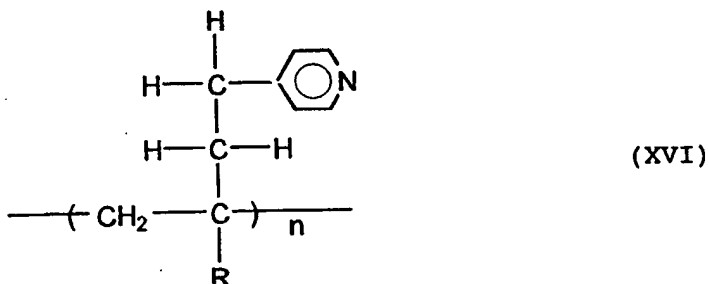
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15

is used, the resulting grafted metallocene catalyzed polymer of formula

20



25

where R may again be hydrogen, branched or straight chain alkyl, carbocyclic, aromatic or heterocyclic. The resulting grafted metallocene catalyzed polymer may be reacted with an acid or acid derivative or a compound of formula  $\text{R}^+\text{X}$ , where

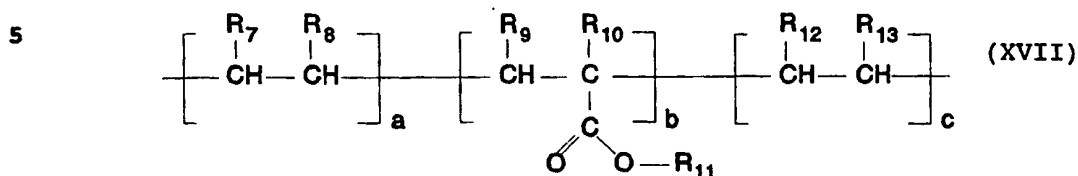
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$\text{R}^+$  may be a linear or branched alkyl group having from 1 to 12 carbon atoms, and X may be a halide, to form a cationic ionomer.

35

Saponified Polymers and Polymer Blends

Saponified polymers useful in the invention can be made from polymers of formula XVII:



10

wherein:

$R_7$  is hydrogen, alkyl such as methyl, ethyl, and branched or straight chain propyl, butyl, pentyl, hexyl, heptyl, and octyl;

15

$R_8$  is hydrogen, lower alkyl including  $C_1-C_5$ , carbocyclic, aromatic or heterocyclic;

$R_9$  is hydrogen, alkyl such as methyl, ethyl and branched or straight chain propyl, butyl, pentyl, hexyl, heptyl and octyl;

20

$R_{10}$  is hydrogen, lower alkyl including  $C_1-C_5$ , carbocyclic, aromatic or heterocyclic;

$R_{11}$  is selected from the group consisting of  $C_nH_{2n+1}$ , for  $n=1$  to 18 (which includes, for example,  $CH_3$ ,  $C_2H_5$ ,  $C_3H_7$ ,  $C_4H_9$ ,  $C_5H_{11}$ ,  $C_6H_{13}$ ,  $C_7H_{15}$ ,  $C_8H_{17}$ ,  $C_9H_{19}$ ,  $C_{10}H_{21}$ ) and phenyl, in which from 0 to 5 H within  $R_{11}$  can be replaced by substituents selected from the group consisting of  $COOH$ ,  $SO_3H$ ,  $NH_2$ , succinic anhydride and their salts, F, Cl, Br, I, OH, SH, epoxy, silicone, lower alkyl esters, lower alkyl ethers, and aromatic or heterocyclic rings, with the proviso that  $R_{10}$  and  $R_{11}$  can be combined to form a bicyclic ring;

25

30

$R_{12}$  is hydrogen, lower alkyl including  $C_1-C_5$ , carbocyclic, aromatic or heterocyclic;

35

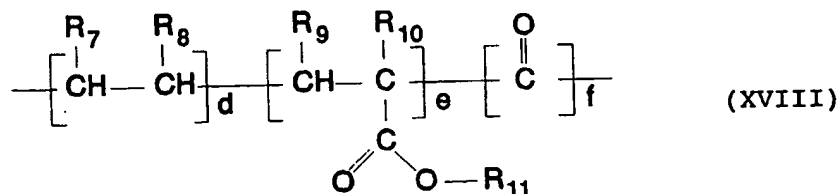
$R_{13}$  is hydrogen, lower alkyl including  $C_1-C_5$ , carbocyclic, aromatic or heterocyclic; and



wherein a, b and c are the relative percentages of each co-monomer.

Saponified polymers can also be formed from polymers of formula XVIII:

5



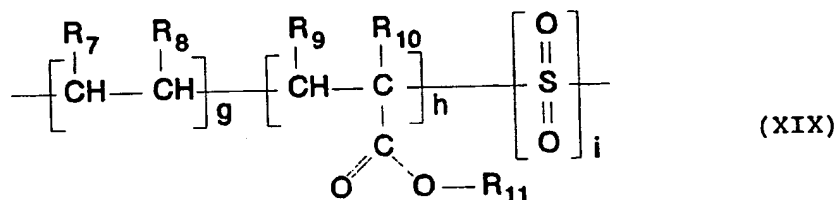
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wherein:

15  $\text{R}_7$ ,  $\text{R}_8$ ,  $\text{R}_9$ ,  $\text{R}_{10}$ , and  $\text{R}_{11}$  are as defined above; and wherein d, e and f are the relative percentages of each co-monomer;

from polymers of formula XIX:

20



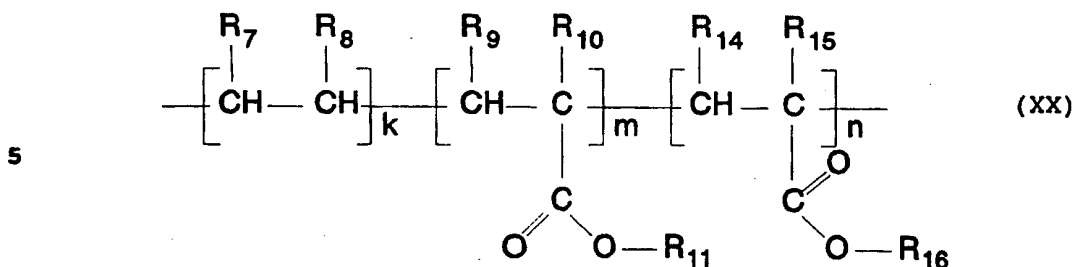
25

wherein:

20  $\text{R}_7$ ,  $\text{R}_8$ ,  $\text{R}_9$ ,  $\text{R}_{10}$ , and  $\text{R}_{11}$  are as defined above; and wherein g, h and i are the relative percentages of each co-monomer;

and from polymers of formula XX:

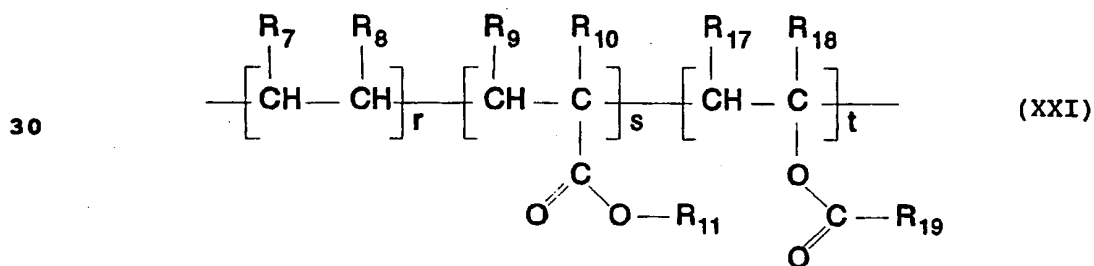
35



10  
 wherein:

R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, and R<sub>11</sub> are as defined above; R<sub>14</sub> is  
 hydrogen, lower alkyl including C<sub>1</sub>-C<sub>5</sub>, carbocyclic,  
 aromatic or heterocyclic; R<sub>15</sub> is hydrogen or lower alkyl  
 15 including C<sub>1</sub>-C<sub>5</sub>; and R<sub>16</sub> is hydrogen, or is selected from  
 the group consisting of C<sub>n</sub>H<sub>2n+1</sub>, for n=1 to 18 and phenyl,  
 in which from 0 to 5 H within R<sub>16</sub> can be replaced by  
 substituents selected from the group consisting of COOH,  
 SO<sub>3</sub>H, NH<sub>3</sub>, succinic anhydride and their salts, F, Cl, Br,  
 20 I, OH, SH, epoxy, silicon, lower alkyl esters, lower  
 alkyl ethers and aromatic or heterocyclic rings, with  
 the proviso that R<sub>15</sub> and R<sub>16</sub> can be combined to form a  
 bicyclic ring; and wherein k, m and n are the relative  
 percentages of each co-monomer.

25 In addition, saponified polymers can be formed from polymers  
 of formula XXI:



35

wherein:

$R_7-R_{11}$  are as defined above;  $R_{17}$  is hydrogen, lower alkyl including  $C_1-C_5$ , carbocyclic, aromatic or heterocyclic;  $R_{18}$  is hydrogen or lower alkyl including  $C_1-C_5$ ; and  $R_{19}$  is hydrogen or is selected from the group consisting of  $C_nH_{2n+1}$  for  $n=1$  to 18 and phenyl, in which from 0 to 5 H within  $R_{19}$  can be replaced by substituents selected from the group consisting of  $COOH$ ,  $SO_3H$ ,  $NH_2$ , succinic anhydride and their salts, F, Cl, Br, I, OH, SH, epoxy, silicone, lower alkyl esters, lower alkyl ethers and aromatic or heterocyclic rings; and  $R_{19}$  is the same as  $R_{16}$ , with the proviso that  $R_{18}$  and  $R_{19}$  can be combined to form a bicyclic ring; and wherein  $r$ ,  $s$  and  $t$  are the relative percentages of each co-monomer.

In each of the polymers described above,  $R_7$  and  $R_8$  can be any combination of alkyl, carbocyclic or aromatic groups, for example, 1-cyclohexylpropyl, benzyl cyclohexylmethyl, 2-cyclohexylpropyl, 2,2-methylcyclohexylpropyl, 2,2-methylphenylpropyl, 2,2-methylphenylbutyl. Comonomer units according to the above formulae are easily manufactured according to techniques and synthetic strategies well known to the skilled artisan. These comonomers are also commercially available from a number of commercial sources.

Saponified polymers can be random, block or alternating polymers and may be made by blending two, three, four, five or more different monomers according to processes well known to one of ordinary skill in the art. Additionally, the subject polymers may be isotactic, syndiotactic or atactic, or any combination of these forms of types of polymers. The pendant groups creating the isotactic, syndiotactic or atactic polymers can be chosen to determine the interactions between the different polymer chains making up the resin to control the final properties of the resins used in golf ball covers. Aromatic and cyclic

olefins can be used in the present invention as well as such specific groups as methyl and phenyl.

The comonomers described herein can be combined in a variety of ways to provide a final copolymer with a variety of characteristics. The letters a, d, g, k, and r represent numbers that can independently range from 1-99 percent, preferably from 10-95 percent, more preferably from 10-70 percent and, most preferably, from about 10-50 percent. The coefficients b, e, h, m and s can independently range from 99-1 percent, preferably from 90-5 percent, more preferably from 90-30 percent, and most preferred from 90-50 percent, and c, f, i, n and t can independently range from 0 to 49 percent.

Graft copolymers of the saponified polymers described above can also be prepared for use in forming golf balls. For example, graft polymers can be produced such that the graft segment making up the linkage between polymer chains comprises an anhydride, wherein "anhydride" is taken to mean a compound having the formula:



wherein:

$\text{R}_{20}$  and  $\text{R}_{21}$  are the same or different and are chosen from among hydrogen, linear or branched chain alkyl and substituted or unsubstituted carboxylic groups. Alternately, however, other grafting agents containing double or triple bonds can be used as grafting agents. Examples of these materials include, but are not limited to, acrylates, styrene and butadiene.

Grafting the polymer molecules of the present invention can be accomplished according to any technique known in the art. See, e.g., Block and Graft Copolymers, by R. Ceresa, pub. by Butterworths, London, U.S. (1962),  
5 incorporated by reference herein. It is preferred that any grafting of the polymers of the present invention be accomplished by adding from about 1 to about 50 percent, or preferably from about 1 to about 25 percent and most preferably from about 1 to about 15 percent of a grafting  
10 agent, such as an anhydride according to Formula XXII above. The grafting agents can be added either as a solid or a non-aqueous liquid, to a polymer according to the present invention. Such post reaction grafting can make the final grafted polymer more flexible.

15       Polymers that can be saponified for use in the present invention can be synthesized by a variety of methods, including metallocene catalysis, since it is well known in the art of polymer synthesis that many different synthetic protocols can be used to prepare a given compound. Different  
20 routes can involve more or less expensive reagents, easier or more difficult separation or purification procedures, straightforward or cumbersome scale-up, and higher or lower yield. The skilled synthetic polymer chemist knows well how to balance the competing characteristics of synthetic  
25 strategies. Thus, the saponified polymers useful in the present invention are not limited by the choice of synthetic strategy, and any synthetic strategy that yields the saponified polymers described above can be used.

      Polymers useful for saponification preferably  
30 comprise: (1) a first monomeric component comprising an olefinic monomer having from 2 to 8 carbon atoms; (2) a second monomeric component comprising an unsaturated carboxylic acid based acrylate class ester having from 4 to 22 carbon atoms; and (3) an optional third monomeric  
35 component comprising at least one monomer selected from the group consisting of carbon monoxide, sulfur dioxide, an anhydride monomer, an unsaturated monocarboxylic acid, an

olefin having from 2 to 8 carbon atoms and a vinyl ester or a vinyl ether of an alkyl acid having from 4 to 21 carbon atoms.

Saponified polymers are preferably prepared by  
5 adding a metal base or metal salt in the form of a solid or a solution to a polymer, such as the polymers described in the previous paragraph. Preferably, however, the metal base is in the form of a solid, such as a powder or a pellet. Powdered bases used in the invention preferably have an  
10 average powder particle diameter of from about 1 to 500 microns. More preferably, such powders have an average particle diameter of 10 to 100 microns. In the case of pellets, substantially any commercially available pellet particle size can be used.

15 Alternately, the metal base can be added in the form of a solution. Preferably, the solution is non-aqueous so that difficulties arising from incomplete removal of water during subsequent processing and use are avoided. Such non-aqueous solutions typically comprise solvents such as  
20 alcohol, acetic acid and acetic anhydride, although other solvents may, of course, be used.

The metal base comprises at least one metallic cation, such as lithium, Li, sodium, Na, potassium, K, cesium, Cs, magnesium, Mg, calcium, Ca, barium, Ba, zinc, Zn,  
25 manganese, Mn, copper, Cu, aluminum, Al, titanium, Ti, tungsten, W, zirconium, Zr, platinum, Pt, rubidium, Rb, and strontium, Sr, and at least one anion, such as hydroxide, alkoxide, acetate, carbonate, bicarbonate, oxide, formate, or nitrate.

30 The polymers described herein are preferably saponified or hydrolyzed by introducing the polymer into an extruder inlet zone, and melting and mixing the polymer in the inlet zone; passing the molten polymer through an addition zone within the extruder downstream from the inlet  
35 zone; and adding a metal base into the molten polymer as it passes through the addition zone. The base may be added to the molten polymer under saponification conditions until the

polymer is at least partially saponified, as indicated by, for example, its melt index or by titrating versus an acid.

However, the metal base is preferably mixed with the polymer under non-saponification conditions. Instead of  
5 simultaneously mixing and saponifying or hydrolyzing as practiced in the prior art, these operations are carried out separately. In the first step, the polymer is heated to a substantially molten state at a temperature typically between about 50-350°C, depending upon the polymer chosen, to  
10 facilitate subsequent mixing with a metal base. This pre-heating step assures a greater degree of homogeneity in the final product, and provides a final product having correspondingly improved properties.

In the next step, the metal base is added to the  
15 molten polymer, and the polymer and metal base are extensively mixed under conditions in which no substantial hydrolysis occurs. A sufficient amount of metal base must be added overall to obtain a degree of saponification of the polymer between about 1 and about 50 percent. The mixing is  
20 carried out at a temperature slightly higher than the melting temperature of the polymer. For mixing on an extruder, the screw speed can be varied between about 20-500 rpm, depending upon the material's viscosity, i.e., the higher the viscosity, the greater the rpm required for proper mixing.  
25 Furthermore, as would be well understood by one of ordinary skill in the art, the depth of the conveying element of the extruder is chosen to prevent substantial hydrolysis of the material during mixing.

Alternately, the mixing may be accomplished using a  
30 roll mill. In such a case, the cylinder roll speed is adjusted to between about 5-100 rpm depending upon the viscosity of the material. Additionally, the mill gap is adjusted as necessary to control the amount of shear, and thus the degree of hydrolysis. The metal base may be added  
35 all at once to the molten polymer, or alternately it may be introduced in batches or stages.

In a third step, conditions are provided such that a hydrolysis or saponification reaction occurs between the polymer and the metal base. Saponification is achieved by continuous mixing of the polymer and base at an elevated  
5 temperature, which is substantially higher than the melting point temperature.

This novel process offers several improvements over the methods disclosed in the prior art. First, it provides for greater ease of mixing of the reactants before the  
10 reaction begins. Because the melt viscosity of the non-salt polymer is much lower than the salt polymer form, the melt mixing of the polymer and metal base is more readily carried out with lower input power requirements. Additionally, mixing of polymer and metal base is more uniform because  
15 there are no substantially hydrolyzed or saponified regions of low melt flow or high melt viscosity present within regions that have not yet reacted and, therefore, have high melt flow and low melt viscosity. Furthermore, the degree of mixing or dispersion of the base in the polymer is more  
20 easily controlled since melt flow rate is more uniform throughout the volume of molten polymer.

Once substantial saponification begins, the reaction is thought to be more uniform than the methods disclosed in the prior art. Although not wishing to be bound  
25 by any particular theory, the controlled dispersion of reactants in the mixing phase is thought to result in a more uniform melt morphology during the hydrolysis phase. The greater ability to control mixing and its uniformity provided by the multi-step process of this invention are thought to  
30 allow a finer morphological texture to develop as the hydrolysis reaction proceeds. That is, smaller size regions arise from dissimilar polarities of the polymer salt formed from hydrolysis and the relatively less polar nonreacted regions and comonomers. Additionally, the morphological  
35 texture that forms is not disrupted by excessive shear mixing. With reduced variation in the size or extent of high and low melt flow rate regions, the melt hydrolysis product



is thought to be more uniform in postsolidification morphology and properties.

This process is preferably accomplished using a twin screw extruder wherein the twin screw extruder comprises melting, addition, and mixing zone means. The process can further be accomplished using a master batch comprising a concentrated amount of metal base in a polymer, with the same or different composition as the polymer introduced into the inlet zone, wherein the master batch is added from a side-stream extruder. The side-stream extruder can be a twin screw extruder comprising melting, addition, and mixing zone means.

Alternatively, the continuous process of saponifying or hydrolyzing the polymers useful in the invention comprises introducing the polymer into an inlet zone of an extruder, and melting and mixing the polymer in the inlet zone; passing the molten polymer through at least two addition zones connected in series; and adding a portion of a metal base into the molten polymer as it passes through each addition zone until the polymer is at least partially saponified.

This process can be accomplished using a twin screw extruder wherein the twin screw extruder comprises melting, addition, and mixing zone means. The process can further be accomplished using a single or a plurality of master batches comprising a concentrated amount of metal base in a polymer, with the same or different composition as the polymer introduced into the inlet zone, and with the same or different amount of metal base as the other master batches, wherein the master batch is added from a side-stream extruder. The process can be accomplished with a single or with multiple side-stream extruders which are twin screw extruders comprising melting, addition, and mixing zone means.

For use in saponified polymer/metallocene catalyzed polymer blends of the present invention, a saponified polymer with ionomeric character can be blended with the other

similar polymers, having a different metal base cation or distribution of cationic species than used to make the first saponified polymer, to yield a blend with desirable golf ball properties. Alternatively, two different saponified polymers with ionomeric character, having the same metal base cation can be blended to yield a useful blend. The two polymers can differ in their degree of hydrolysis, degree of subsequent acidification, molecular weight, molecular weight distribution, tacticity, blockiness, etc.

10

#### Saponified Polymer/Metallocene Catalyzed Polymer Blends

The saponified polymer/metallocene catalyzed polymer blends of the present invention may be used alone or blended with other polymers or ionomers, according to methods well known in the art, to form compositions useful for forming golf balls.

For example, the saponified polymer/metallocene catalyzed polymer blends of the present invention may be combined with thermoplastic ionomers, such as ethylene methacrylic acid ionomers and ethylene acrylic acid ionomers and their terpolymers, which are sold commercially under the trade names SURLYN® and IOTEK® by DuPont and Exxon respectively.

The saponified polymer/metallocene catalyzed polymer blends of the present invention may also be combined with other non-ionic thermoplastics. Polymers of this type which can be used in conjunction with the polymers of the claimed invention in golf ball covers include:

poly(ethylethylene), poly(heptylethylene),  
poly(hexyldecylethylene), poly(isopentylethylene),  
poly(1,1-dimethyltrimethylene),  
poly(1,1,2-trimethyltrimethylene), poly(butyl acrylate),  
poly(4-cyanobutyl acrylate), poly(2-ethylbutyl acrylate),  
poly(heptyl acrylate), poly(2-methylbutyl acrylate),  
poly(3-methylbutyl acrylate), poly(N-octadecylacrylamide),  
poly(octadecyl methacrylate), poly(butoxyethylene),  
poly[1,1-bis(trifluoromethoxy)difluoroethylene],

- poly(methoxyethylene), poly(pentyloxyethylene),  
 poly(1,1-dichloroethylene), poly(cyclopentylacetoxyethylene),  
 poly(4-[(2-butoxyethoxy)methyl]styrene),  
 poly(4-dodecylstyrene), poly(4-tetradecylstyrene),  
 5 poly(phenethylmethylethylene),  
 poly[oxy(allyloxymethyl)ethylene],  
 poly[oxy(ethoxymethyl)ethylene], poly(oxyethylethylene),  
 poly(oxytetramethylene), poly(oxytrimethylene),  
 poly(oxycarbonylpentamethylene),  
 10 poly(oxycarbonyl-3-methylpentamethylene),  
 poly(oxycarbonyl-1,5-dimethylpentamethylene),  
 poly(oxy-2,2,3,3,4,4-hexafluoropentamethyleneoxyadipoyl),  
 poly[oxy(methyl)-3,3,3-trifluoropropylsilylene-  
 3p3-difluoropentamethylene(methyl)-  
 15 3,3,3-trifluoropropylsilylene], poly(silanes) and  
 poly(silazanes), main-chain heterocyclic polymers and  
 poly(furan tetracarboxylic acid diimides) as well as the  
 classes of polymers to which they belong.

- More preferably, the other polymers that can be  
 20 used in conjunction with saponified polymer/metallocene  
 catalyzed polymer blends in golf ball covers include: block  
 copolymers of a poly(ether-ester), such as HYTREL® available  
 from DuPont, block copolymers of a poly(ether-amide), such as  
 PEBAX® available from Elf Atochem, styrene-butadiene-styrene  
 25 block copolymers, such as the KRATON D® grades available from  
 Shell Chemical, styrene-(ethylene-propylene)-styrene or  
 styrene-(ethylene-butylene)-styrene block copolymers, such as  
 the KRATON G® series from Shell Chemical, either of the  
 KRATON®s with maleic anhydride or sulfonic graft or  
 30 functionality, such as the KRATON FD® or KRATON FG® series  
 available from Shell Chemical, olefinic copolymers, such as  
 the ethylene-acrylate or ethylene methacrylate series  
 available from Quantum, ethylene-octene copolymers made from  
 metallocene catalysts, such as the AFFINITY® or ENGAGE®  
 35 series available from Dow, ethylene-alpha olefin copolymers  
 and terpolymers made from metallocene catalysts, such as the  
 EXACT® series available from Exxon, block

poly(urethane-ester) or block poly(urethane-ether) or block poly(urethane-caprolactone), such as the ESTANE series available from BF Goodrich, polyethylene glycol, such as CARBOWAX available from Union Carbide, polycaprolactone, 5 polycaprolactam, polyesters, such as EKTAR available from Eastman, polyamides, such as nylon 6 or nylon 6,6, available from DuPont and ICI, ethylene-propylene-(diene monomer) terpolymers and their sulfonated or carboxylated derivatives, and SANTOPRENE from Monsanto.

10       The saponified polymer/metallocene catalyzed polymer blends of the present invention can be prepared with or without the addition of a compatibilizer, and with varying molecular architecture of blend components, such as varying molecular weight, tacticity, degrees of blockiness, etc., as 15 is well known to those knowledgeable in the art of blending polymers.

          The amounts of polymers used in the present invention can vary from 1 to 99 parts of the saponified polymer/metallocene catalyzed polymer blend to 99 to 1 parts 20 of other polymers or ionomers, based on the total weight of polymers. More preferred ratios of 95 to 5 parts of the saponified polymer/metallocene catalyzed polymer blend with 5 to 95 parts of one or more other polymers. Most preferred is from about 95 to about 10 parts of the subject saponified 25 polymer/metallocene catalyzed polymer blends and from about 5 to about 90 parts of the other polymer or ionomer.

          Blending of the saponified polymer/metallocene catalyzed polymer blends is accomplished in a conventional manner using conventional equipment. Good results have been 30 obtained by mixing the comonomers or resins in a solid, pelletized form and then placing the mix into a hopper which is used to feed the heated barrel of the injection molding machine. Further mixing is accomplished by a screw in the heated barrel. The injection molding machine is used either 35 to make preformed half-shells for compression molding about a core or for molding flowable cover stock about a core using a retractable-pin mold. Such machines are conventional.

Additional components which can be added to the golf ball compositions of the present invention include U.V. stabilizers, reactive and non-reactive fillers, white pigments, e.g.,  $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{BaSO}_4$ , colored pigments, 5 fluorescent pigments, optical brighteners, and light stabilizers.

The present polymers may be blended with any of the additional ingredients noted above, for example, to be used in a golf ball cover using any conventional blending 10 technique. For example, the present compounds may be added to a vessel containing pelletized polymer resins and heated to  $300^\circ\text{F}$ - $500^\circ\text{F}$ . Thorough mixing of the materials is accomplished by means of a screw in the heated vessel.

The saponified polymer/metallocene catalyzed 15 polymer blends of the invention can be used to form any type of golf ball. In particular, two-piece golf balls comprising a cover surrounding a core are within the scope of the present invention, as are wound golf balls, in which a liquid, semi-solid or solid core is surrounded by an elastic 20 synthetic material. The term "solid cores" as used herein refers not only to one piece cores but also to those cores having a separate solid layer beneath the cover and above the core, and other multilayer and/or non-wound cores. Any type of golf ball core can be used in the golf balls of the 25 present invention. Preferred cores, however, include some amount of cis-polybutadiene. The subject polymers may also be used in golf balls having multiple covers and/or multiple cores.

Typically, the covers are formed around the solid 30 or wound cores by either compression molding preformed half-shells of the cover stock material or by injection molding the cover stock about the core. Half-shells are made by injection molding a cover stock into a conventional half-shell mold in a conventional manner. The preferred 35 method is compression molding of preformed half-shells.

In compression molding, the half-shells of the stock material are formed by injection molding the cover

stock material into a conventional half-shell mold, typically at 300°F-520°F for a short time. The preformed half-shells are then placed about a core and the assembly is introduced into a compression molding machine, and compression molded about a core, typically at about 250 to 400°F. The compression molding machine is a hydraulic press having an upper and lower mold plate, which have half molds, each of which is registered with another half mold in the opposite mold plate. The molded balls are then cooled while still in the mold, and finally removed when the cover is hard enough to be handled without deforming.

Alternatively, golf balls can be covered solely with the use of an injection molding technique. In injection molding, an injection molding machine is utilized in which the core assembly is placed in a mold cavity. The core assembly is held in place through the use of several retractable pins. Such injection molding machines are well known in the art. The molten cover material is injected into the cavity surrounding the core. As the cover material cools and hardens, the pins retract and the molded ball is ejected from the mold. The balls then undergo conventional finishing operations such as buffing, painting and stamping. This type of cover construction is generally referred to as a one-piece cover.

The present invention can be used in forming golf balls of any desired size. While "The Rules of Golf" by the USGA dictates that the size of a competition golf ball be no less than 1.680 inches in diameter, golf balls of any size can be used for leisure golf play. The preferred diameter of the golf balls is from about 1.680 inches to about 1.800 inches. The more preferred diameter is from about 1.680 inches to about 1.760 inches. A diameter of from about 1.680 inches to about 1.740 inches is most preferred, however diameters anywhere in the range of from 1.680 to about 1.95 inches can be used. Oversize golf balls above about 1.760 inches to golf balls having diameters as big 2.75 inches are also within the scope of the present invention.

While it is apparent that the invention disclosed herein is well calculated to fulfill the objects stated above, it will be appreciated that numerous modifications and embodiments may be devised by those skilled in the art.

5 Therefore, it is intended that the appended claims cover all such modifications and embodiments that fall within the true spirit and scope of the present invention.

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## THE CLAIMS

I claim:

1. A golf ball having least one layer, the layer  
5 formed of a saponified polymer/metallocene catalyzed polymer  
blend, comprising from about 1 to about 99 parts of at least  
one saponified polymer and from about 99 to 1 parts of at  
least one metallocene catalyzed polymer, based on 100 parts  
by weight of the saponified polymer/metallocene catalyzed  
10 polymer blend.
2. The golf ball according to claim 1, further  
comprising a cover, wherein the layer forms at least a  
portion of the cover.
- 15 3. The golf ball according to claim 2, wherein the  
layer has a foamed structure.
4. The golf ball according to claim 1, comprising  
20 a core, wherein the layer forms at least a portion of the  
core.
5. The golf ball according to claim 1, further  
comprising a wound core.
- 25 6. The golf ball according to claim 5, wherein the  
layer has a foamed structure.
7. The golf ball according to claim 1, further  
30 comprising a cover and a core and a mantle situated between  
the cover and the core.
8. The golf ball according to claim 7, wherein the  
core is a wound core.
- 35 9. The golf ball according to claim 8, wherein the  
layer forms at least a portion of the mantle.

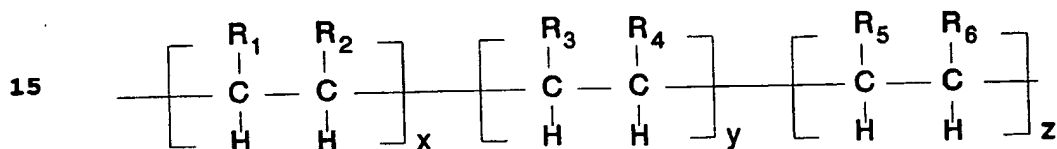


10. The golf ball according to claim 9, wherein the layer has a foamed structure.

11. The golf ball according to claim 1, wherein the metallocene catalyzed polymer is chosen from the group consisting of olefinic homopolymers and copolymers of ethylene with propylene, butene, hexene, octene, and norbornene, and olefinic homopolymers and copolymers of propylene with butene, hexene, octene, and norbornene.

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12. The golf ball according to claim 1, wherein the metallocene catalyzed polymer is of the formula:



wherein

20  $R_1$  is hydrogen;

$R_2$  is hydrogen or lower alkyl selected from the group consisting of  $CH_3$ ,  $C_2H_5$ ,  $C_3H_7$ ,  $C_4H_9$ , and  $C_5H_{11}$ ;

$R_3$  is hydrogen or lower alkyl selected from the group consisting of  $CH_3$ ,  $C_2H_5$ ,  $C_3H_7$ ,  $C_4H_9$ , and  $C_5H_{11}$ ;

25  $R_4$  is selected from the group consisting of H,  $CH_3$ ,  $C_2H_5$ ,  $C_3H_7$ ,  $C_4H_9$ ,  $C_5H_{11}$ ,  $C_6H_{13}$ ,  $C_7H_{15}$ ,  $C_8H_{17}$ ,  $C_9H_{19}$ ,  $C_{10}H_{21}$ , and phenyl, in which from 0 to 5 H within  $R_4$  can be replaced by substituents selected from the group consisting of  $COOH$ ,  $SO_3H$ ,  $NH_2$ , F, Cl, Br, I, OH, SH, silicone, lower alkyl esters and lower alkyl  
30 ethers, with the proviso that  $R_3$  and  $R_4$  can be combined to form a bicyclic ring;

$R_5$  is hydrogen, lower alkyl including  $C_1-C_5$ , carbocyclic, aromatic or heterocyclic;

$R_6$  is hydrogen, lower alkyl including  $C_1-C_5$ , carbocyclic,

35 aromatic or heterocyclic; and

wherein x ranges from 99 to 50 weight per cent of the polymer, y ranges from 1 to 50 weight per cent of the polymer and z ranges from 0 to 49 weight per cent of the polymer.

5           13. The golf ball according to claim 1, wherein the saponified polymer comprises a first olefinic, monomeric component having from 2 to 8 carbon atoms and a second monomeric component comprising an unsaturated carboxylic acid based acrylate class ester having from 4 to 22 carbon atoms  
10 and at least one ester group, wherein at least a portion of the ester groups have been saponified with an inorganic metal base.

          14. The golf ball according to claim 13, wherein  
15 the metal base comprises at least one metallic cation, selected from the group consisting of lithium, sodium, potassium, cesium, magnesium, calcium, barium, manganese, copper, zinc, aluminum, titanium, tungsten, zirconium, platinum, rubidium, and strontium, and at least one anion,  
20 selected from the group consisting of hydroxide, alkoxide, acetate, carbonate, bicarbonate, oxide, formate, and nitrate.

          15. The golf ball according to claim 13, wherein the first monomeric component comprises an  $\alpha$ -olefin monomer  
25 having a terminal point of unsaturation.

          16. The golf ball according to claim 15, wherein the first monomeric component has the formula:



wherein:

$R_7$  is hydrogen or an alkyl group; and  
           $R_8$  is hydrogen, lower alkyl including  $C_1$ - $C_5$ ;  
35 carbocyclic, aromatic or heterocyclic.

17. The golf ball according to claim 16, wherein the first monomeric component is ethylene.

18. The golf ball according to claim 13, wherein the first monomeric component comprises from about 1 to about 99 percent by weight of the total polymer weight.

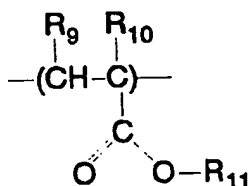
19. The golf ball according to claim 13, wherein the first monomeric component comprises from about 10 to about 95 percent by weight of the total polymer weight.

20. The golf ball according to claim 13, wherein the first monomeric component comprises from about 10 to about 70 percent by weight of the total polymer weight.

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21. The golf ball according to claim 12, wherein the second monomeric component is an unsaturated acrylate class ester having the formula:

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wherein:

$R_9$  is hydrogen or an alkyl group;

$R_{10}$  is hydrogen, lower alkyl including  $C_1-C_3$ , carbocyclic, aromatic or heterocyclic;

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$R_{11}$  is selected from the group consisting of  $C_nH_{2n+1}$ , for  $n=1$  to 18 and phenyl, in which from 0 to 5 H within  $R_{10}$  can be replaced by substituents selected from the group consisting of  $\text{COOH}$ ,  $\text{SO}_3\text{H}$ ,  $\text{NH}_2$ , succinic anhydride and their salts, F, Cl, Br, I, OH, SH, epoxy, silicone, lower alkyl esters, lower alkyl ethers, and aromatic or heterocyclic rings with the proviso that  $R_{10}$  and  $R_{11}$  can be combined to form a bicyclic ring.

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22. The golf ball according to claim 21, wherein the second monomeric component comprises from about 99 to about 1 percent by weight of the total polymer weight.

5           23. The golf ball according to claim 21, wherein the second monomeric component comprises from about 90 to about 5 percent by weight of the total polymer weight.

10           24. The golf ball according to claim 21, wherein the second monomeric component comprises from about 90 to about 30 percent by weight of the total polymer weight.

25. The golf ball according to claim 12, further comprising a third monomeric component selected from the  
15 group consisting of carbon monoxide, sulfur dioxide, an anhydride monomer, an unsaturated monocarboxylic acid, an olefin having from 2 to 8 carbon atoms and a vinyl ester or a vinyl ether of an alkyl acid having from 4 to 21 carbon atoms.

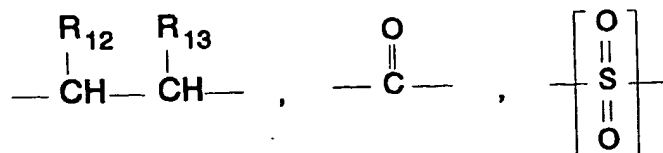
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26. The golf ball according to claim 25, wherein the third monomeric component is at least one of the monomers selected from the group consisting of:

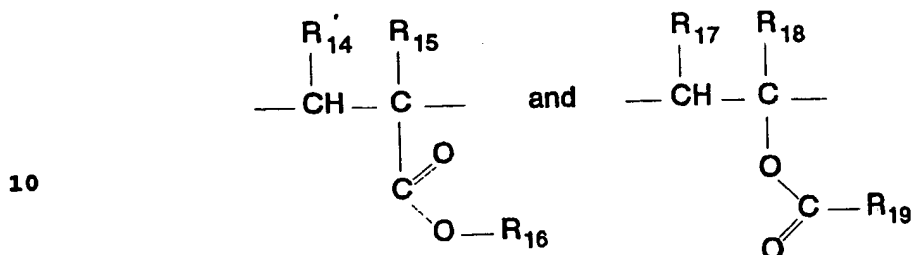
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15 wherein:

$R_{12}$  is hydrogen, lower alkyl including  $C_1-C_5$ , carbocyclic, aromatic or heterocyclic;

$R_{13}$  is hydrogen, lower alkyl including  $C_1-C_5$ , carbocyclic, aromatic or heterocyclic;

20  $R_{14}$  is hydrogen, lower alkyl including  $C_1-C_5$ , carbocyclic, aromatic or heterocyclic;

$R_{15}$  is hydrogen or lower alkyl including  $C_1-C_5$ ;

25  $R_{16}$  is hydrogen, or is selected from the group consisting of  $C_nH_{2n+1}$ , for  $n=1$  to 18 and phenyl, in which from 0 to 5 H within  $R_{16}$  can be replaced by substituents selected from the group consisting of  $COOH$ ,  $SO_3H$ ,  $NH_2$ , and their salts, F, Cl, Br, I, OH, SH, silicon, lower alkyl esters, lower alkyl ethers and aromatic or heterocyclic rings with the proviso that  $R_{15}$  and  $R_{16}$  can be combined to

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form a bicyclic ring;

$R_{17}$  is hydrogen, lower alkyl including  $C_1-C_5$ , carbocyclic, aromatic or heterocyclic;

$R_{18}$  is hydrogen or lower alkyl including  $C_1-C_5$ ;

35  $R_{19}$  is hydrogen, or is selected from the group consisting of  $C_nH_{2n+1}$ , for  $n=1$  to 18 and phenyl, in which from 0 to 5 H within  $R_{19}$  can be replaced by substituents

selected from the group consisting of COOH, SO<sub>3</sub>H, NH<sub>2</sub> and their salts, F, Cl, Br, I, OH, SH, silicon, lower alkyl esters, lower alkyl ethers and aromatic or heterocyclic rings with the proviso that R<sub>18</sub> and R<sub>19</sub> can be combined to  
5 form a bicyclic ring.

27. The golf ball according to claim 25, wherein the third monomeric component comprises from about 0 to 49 percent by weight of the total polymer weight.  
10

28. The golf ball according to claim 13, wherein the monomeric components of the polymer are present in a random, alternating, block or graft arrangement.

29. The golf ball according to claim 13, wherein the polymer is of a form selected from the group consisting of isotactic, syndiotactic, and atactic polymers and combinations thereof.  
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30. The golf ball according to claim 1, wherein a grafting agent has been added to at least one of the saponified polymer or the metallocene catalyzed polymer to form a grafted polymer.  
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31. The golf ball according to claim 30, wherein the grafting agent comprises an anhydride having the formula:



wherein:

10  $R_{20}$  and  $R_{21}$  are the same or different and are selected from the group consisting of hydrogen, linear or branched chain alkyl and substituted or unsubstituted carboxylic groups.

15 32. The golf ball according to claim 30, wherein the grafting agent is added in an amount of between about 1-50 percent by weight of the polymer.

20 33. The golf ball according to claim 30, wherein the grafting agent is added in an amount of between about 1-25 percent by weight of the polymer.

25 34. The golf ball according to claim 30, wherein the grafting agent is added in an amount of between about 1-15 percent by weight of the polymer.

30 35. A golf ball comprising a cover and a core and a mantle situated between the cover and the core, wherein at least one of the cover, the core, and the mantle comprises at least one layer, the layer formed of a saponified polymer/metallocene catalyzed polymer blend, comprising from about 1 to about 99 parts of at least one saponified polymer and from about 99 to 1 parts of at least one metallocene catalyzed polymer, based on 100 parts of the saponified polymer/metallocene catalyzed polymer blend.

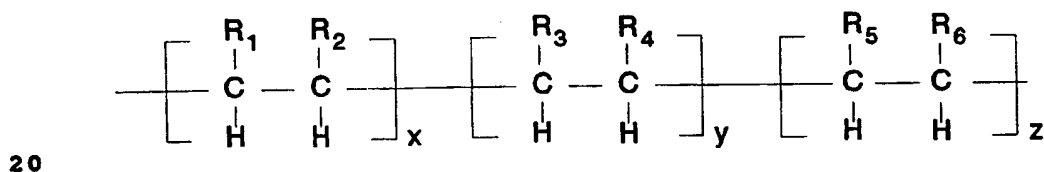
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36. The golf ball according to claim 35, wherein the core is a wound core.

37. The golf ball according to claim 36, wherein the layer has a foamed structure.

38. The golf ball according to claim 36, wherein the metallocene catalyzed polymer is chosen from the group consisting of copolymers of ethylene with propylene, butene, hexene, octene, and norbornene, and homopolymers and copolymers of propylene with butene, hexene, octene, and norbornene.

39. The golf ball according to claim 36, wherein the metallocene catalyzed polymer is of the formula:



wherein

$R_1$  is hydrogen;

25  $R_2$  is hydrogen or lower alkyl selected from the group consisting of  $CH_3$ ,  $C_2H_5$ ,  $C_3H_7$ ,  $C_4H_9$ , and  $C_5H_{11}$ ;

$R_3$  is hydrogen or lower alkyl selected from the group consisting of  $CH_3$ ,  $C_2H_5$ ,  $C_3H_7$ ,  $C_4H_9$ , and  $C_5H_{11}$ ;

30  $R_4$  is selected from the group consisting of H,  $CH_3$ ,  $C_2H_5$ ,  $C_3H_7$ ,  $C_4H_9$ ,  $C_5H_{11}$ ,  $C_6H_{13}$ ,  $C_7H_{15}$ ,  $C_8H_{17}$ ,  $C_9H_{19}$ ,  $C_{10}H_{21}$ , and phenyl, in which from 0 to 5 H within  $R_4$  can be replaced by substituents selected from the group consisting of  $COOH$ ,  $SO_3H$ ,  $NH_2$ , F, Cl, Br, I, OH, SH, silicone, lower alkyl esters and lower alkyl ethers, with the proviso that  $R_3$  and  $R_4$  can be combined to

35 form a bicyclic ring;

$R_5$  is hydrogen, lower alkyl including  $C_1$ - $C_3$ , carbocyclic, aromatic or heterocyclic;



$R_6$  is hydrogen, lower alkyl including  $C_1-C_3$ , carbocyclic, aromatic or heterocyclic; and  
wherein x ranges from 99 to 50 weight per cent of the polymer, y ranges from 1 to 50 weight per cent of the polymer  
5 and z ranges from 0 to 49 weight per cent of the polymer.

40. The golf ball according to claim 36, wherein the saponified polymer comprises a first olefinic, monomeric component having from 2 to 8 carbon atoms and a second  
10 monomeric component comprising an unsaturated carboxylic acid based acrylate class ester having from 4 to 22 carbon atoms and at least one ester group, wherein at least a portion of the ester groups have been saponified with an inorganic metal base.

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41. A process for forming a golf ball, which comprises:

forming a polymer comprising a first olefinic monomeric component having from 2 to 8 carbon atoms and a second  
20 monomeric component comprising an unsaturated carboxylic acid based acrylate class ester having from 4 to 22 carbon atoms;

applying a sufficient amount of heat to the polymer to convert the polymer to a substantially molten state;

forming a mixture by adding an inorganic metal base to  
25 the molten polymer, such that the viscosity of the mixture remains substantially unchanged from the viscosity of the molten polymer;

saponifying the mixture to form a saponified polymer, wherein a sufficient amount of the inorganic metal base  
30 is added to the molten polymer in forming the mixture to obtain a degree of saponification of the polymer ranging between about 1 and 50 percent;

blending the saponified polymer with a metallocene catalyzed polymer to form a saponified polymer/metallocene  
35 catalyzed polymer blend; and

forming at least one layer of a golf ball from the saponified polymer/metallocene catalyzed polymer blend.

42. The process according to claim 41, wherein the polymer further comprises a third monomeric component, selected from the group consisting of carbon monoxide, sulfur dioxide, an anhydride monomer, an unsaturated monocarboxylic acid, an olefin having from 2 to 8 carbon atoms, and a vinyl ester or a vinyl ether of an alkyl acid having from 4 to 21 carbon atoms.

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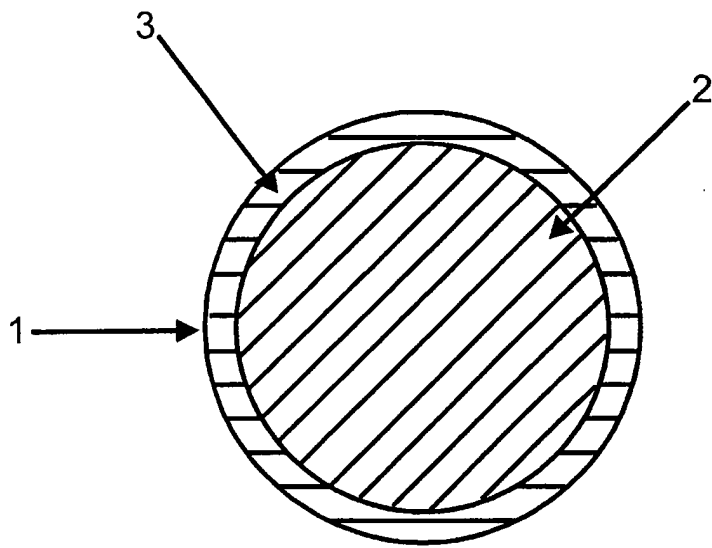


FIGURE 1

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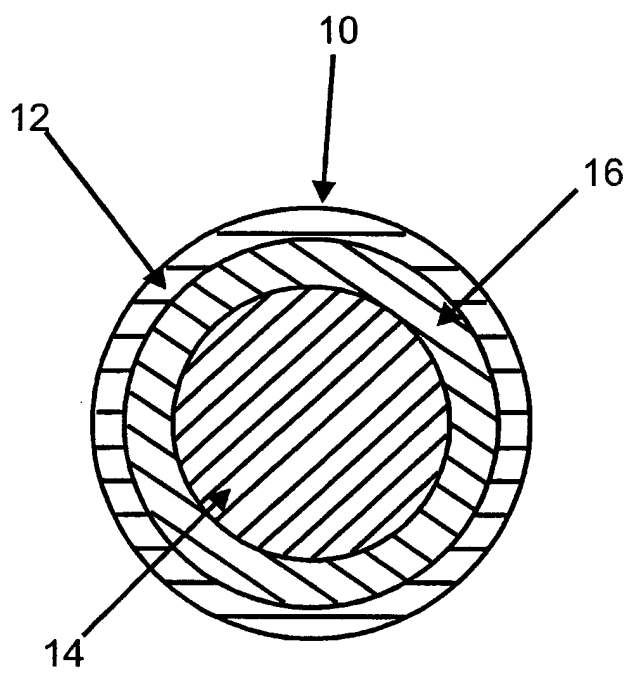


FIGURE 2

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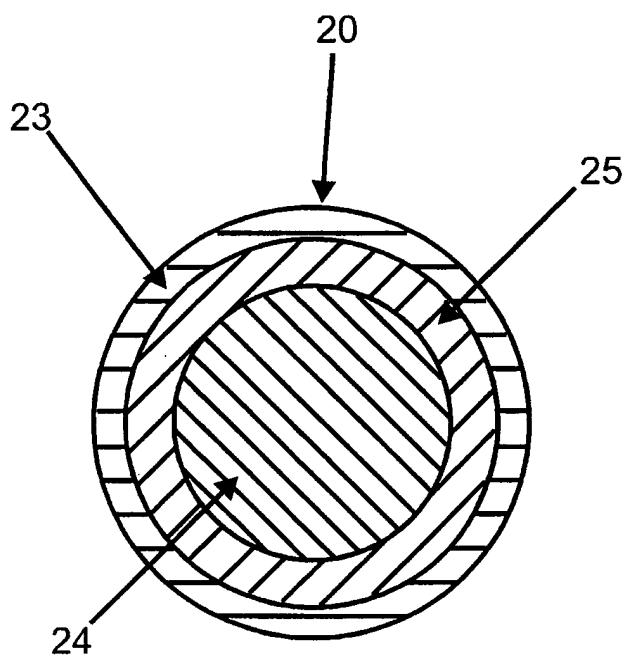


FIGURE 3

## INTERNATIONAL SEARCH REPORT

 International application No.  
PCT/US99/08080

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : A63B 37/12, 37/02, 37/04

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 473/355, 365, 371, 372, 373, 378, 385; 521/134; 525/72, 74, 196, 201, 221

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97/19114 A (ACUSHNET COMPANY) 29 May 1997, page 23 lines 7-28.	1, 2, 5, 7-9, 11-36 and 38-42
Y		3, 4, 6, 10 and 37
Y,P	US 5,824,746 A (HARRIS et al) 20 October 1998, tables I-VII.	1-42
Y	WO 96/40382 A (ACUSHNET COMPANY) 19 December 1996, tables I-VII.	1, 2, 5, 7-9, 11-36 and 38-42
Y	US 4,638,034 A (MCCLAIN) 20 January 1987, col. 1 lines 21-30, col. 3 lines 19-25.	1-42



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

11 MAY 1999

Date of mailing of the international search report

27 MAY 1999

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**INTERNATIONAL SEARCH REPORT**

International application No.  
PCT/US99/08080

**A. CLASSIFICATION OF SUBJECT MATTER:**

US CL :

473/355, 365, 371, 372, 373, 378, 385; 521/134; 525/72, 74, 196, 201, 221

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